The Calculation of Matrix Elements in Relativistic Quantum Mechanics

A. C. Ilarraza-Lomelí, M. N. Valdés-Martínez, A. L. Salas-Brito*
Laboratorio de Sistemas Dinámicos, Departamento de Ciencias Básicas,
Universidad Autónoma Metropolitana-Azcapotzalco.
Apartado Postal 21–267, Coyoacán, Mexico City, Distrito Federal C. P. 04000 México.

R. P. Martínez-y-Romero†
Facultad de Ciencias, Universidad Nacional Autónoma de México,
Apartado Postal 50-542, México City, Distrito Federal C. P. 04510 México.

H. N. Núñez-Yépez‡
Departamento de Física, Universidad Autónoma Metropolitana-Iztapalapa
Apartado Postal 55–534, Iztapalapa, Distrito Federal C. P. 09340 México.

Abstract.

Employing a relativistic version of a hypervirial result, recurrence relations for arbitrary non-diagonal radial hydrogenic matrix elements have recently been obtained in Dirac relativistic quantum mechanics. In this contribution honoring Professor Löwdin, we report on a new relation we have recently discovered between the matrix elements $\langle 2|r^\lambda|1\rangle$ and $\langle 2|\beta r^\lambda|1\rangle$—where β is a Dirac matrix and the numbers distiguish between different radial eigenstates— that allow for a simplification and hence for a more convenient way of expressing the recurrence relations. We additionally derive another relation that can be employed for simplifying two center matrix element calculations in relativistic atomic or molecular calculations.

Keywords: Relativistic hydrogen atom, relativistic recurrence relations, non-diagonal matrix elements, two-center matrix elements, hypervirial relations.

PACS: 3.65.Ca

* Corresponding author, e-mail: asb@data.net.mx or asb@correo.azc.uam.mx
† e-mail: rodolfo@dirac.fciencias.unam.mx
‡ e-mail: nyhn@xanum.uam.mx

Introduction

The evaluation of expectation values is always required for relating quantum calculations to experimental results in atomic or molecular physics. In most cases such expectation values can be expressed as matrix elements of powers of a radial coordinate r; this comes about since these powers can be regarded as either exact terms in a certain potential (as in the Lennard-Jones, the Casimir or the London potentials) or as terms in a multipolar expansion of the interaction with the electromagnetic field [1–5]. Matrix elements of that sort can be also regarded as starting points of certain useful approximation schemes, like variational or Hartree-Fock or configuration interaction methods, to which the late Professor Löwdin made important contributions [6–14] and which admit relativistic extensions [15–17]. The treatment of electromagnetic interactions in the realm of multiphoton transitions in very intense laser fields usually needs a full quantum electrodynamics treatment [1], but this is time consuming. As a good approximation we can use instead the relativistic Dirac quantum mechanical formalism [2]. One has only to remember the successes this theory has achieved in dealing with the hydrogen atom [18,19]. One can start with the known states of the relativistic hydrogen atom [18,20–23] and then proceed, as in non-relativistic quantum mechanics, to expand the states of interest in terms of the former [24]. The problem is thus reduced to the evaluation of matrix elements of powers of r between relativistic eigenstates of the hydrogen atom—a much simpler problem. The bad news are that these evaluations also become cumbersome. This calls for techniques adroit for evaluating them. In nonrelativistic quantum mechanics these techniques in the form of algebraic methods, recurrence relations or clever uses of hypervirial theorems abound (see, for example,[25–31], but in the relativistic domain they are rather scarse (but see [4,32–34]). Such lack of techniques is also manifest in the non existence of relations valid for two center matrix elements.

The matrix elements of different powers of r between Dirac eigenstates of the hydrogen atom referred to above require the evaluation the following type of integrals

$$\begin{aligned}
\langle n_2\, j_2\, \epsilon_2|f(r)|n_1\, j_1\, \epsilon_1\rangle &= \int f(r)\,(F_2^*(r)F_1(r)+G_2^*(r)G_1(r))\,dr,\\
\langle n_2\, j_2\, \epsilon_2|\beta f(r)|n_1\, j_1\, \epsilon_1\rangle &= \int f(r)\,(F_2^*(r)F_1(r)-G_2^*(r)G_1(r))\,dr,
\end{aligned} \tag{1}$$

where $f(r)$ is any function of r, the kets $|n\, j\, \epsilon\rangle$ stand for a bispinorial Dirac radial eigenstate of the hydrogen atom and the subscripts label different states. Any of such states, when projected on the $|r\rangle$ basis, become [2]

$$\langle r|n\,j\,\epsilon\rangle = \frac{1}{r}\begin{pmatrix} F_{nj\epsilon}(r) \\ \\ iG_{nj\epsilon}(r) \end{pmatrix}. \tag{2}$$

In equation (1) we used the shorthand $F_k = F_{n_k j_k \epsilon_k}(r)$ and $G_k = G_{n_k j_k \epsilon_k}(r)$, that are called, respectively, the big and small components of the bispinor (2), and that are the solutions of the radial Dirac equation. This radial equation can be written [35] as $(H_k - E_k)\psi_k(r) = 0$, where the E_k are the energy eigenvalues,

$$H_k = c\alpha_r[p_r - i\beta\epsilon_k(j_k + 1/2)/r] + \beta c^2 + V_k(r), \tag{3}$$

is the radial Dirac Hamiltonian, k is just a label —useful in what follows—, and $\beta =$ diag$(1, -1)$ is a Dirac matrix (for a pedagogical discussion of the radial equation and of the hydrogen atom in Dirac quantum mechanics see [36]), and [37–38]

$$\alpha_r = \begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix}, \quad \text{and} \quad p_r = -i\left(\frac{1}{r} + \frac{d}{dr}\right). \tag{4}$$

Writing the radial equation in a more explicit form, we have

$$\begin{bmatrix} c^2 + V_k(r) - E_k & c\epsilon_k\,(j_k + 1/2)\,/r - cd/dr \\ \\ c\epsilon_k\,(j_k + 1/2)\,/r + cd/dr & -c^2 + V_k(r) - E_k \end{bmatrix} \begin{bmatrix} F_{n_k j_k \epsilon_k}(r) \\ \\ G_{n_k j_k \epsilon_k}(r) \end{bmatrix} = 0, \tag{5}$$

where $n = 0, 1, 2, \ldots$ is the principal quantum number, $j = 1/2, 3/2, 5/2, \ldots$ the total (orbital plus spin) angular momentum quantum number, $\epsilon \equiv (-1)^{j+l-1/2}$, $l\,(= j \pm 1/2$, according to whether l refers to the big or to the small component of the hydrogenic spinor) is the orbital angular momentum quantum number, and $V_k(r)$ is any radial potential (of scalar type). Please note that here as in all of the paper we are using atomic units: $m_e = e = \hbar = 1$. The quantum number ϵ equals $+1$ when $l = j + 1/2$ and equals -1 when $l = j - 1/2$ and it is related to the often used eigenvalue, κ, of the operator $\beta(1 + \mathbf{\Sigma}\cdot\mathbf{L})$ by $\kappa = -\epsilon(j + 1/2)$, where $\Sigma \equiv$ diag$(\boldsymbol{\sigma}, \boldsymbol{\sigma})$ and $\boldsymbol{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$ is the usual 3-vector spin operator. Notice also that, as in equations (2), (4), and (5) above, we can work in the somewhat easier to handle 2 dimensional subspace of the 4-dimensional Dirac operators. This choice has no relevance whatsoever for the final results. Closed forms for the integrals (1) or certain approximations thereof have been given in the Appendix of [38] and in [34,39,40] but even these become very cumbersome for many uses.

On trying to overcome the complications mentioned above, recurrence relations which can be used to compute general —not necessarily diagonal— matrix elements between relativistic hydrogenic states of r^λ have recently been obtained

[37,38]. Given such recursions, it is only needed to evaluate at most 6 matrix elements, 3 for r^λ and 3 more for βr^λ, for obtaining every other matrix element of r^λ or of βr^λ between hydrogenic states.

In this contribution honoring the memory of Professor Löwdin and his work, we want to review these recurrence relations and to discuss one more relation, previously unnoticed to us, which can greatly simplify the use of the recurrence relations already reported. Other purpose of this contribution is to derive an hypervirial-like formula that can be useful for evaluating relativistic two center matrix elements.

The previously known recurrence relations

The recurrence formulae have been obtained rederiving in the relativistic realm a non-relativistic hypervirial result previously used to derive the Blanchard recursion relations between hydrogenic matrix elements of r^α terms [41,42]. The non-relativistic Blanchard relation has been found so interesting that it has been generalized [39]. We have to point out that our relativistic approach is totally different from Blanchard's; we start constructing an hypervirial and then proceed with several relativistic identities that have led us to the recurrence relations we are after [37,38]. This approach is inspired in a technique previously employed for similar purposes in non-relativistic quantum mechanics [41].

To obtain a relativistically valid recurrence relation, let us first compute matrix elements of the radial function $\xi(r) = H_2 f(r) - f(r) H_1$, where H_i is one of the Hamiltonians—these are really the same Hamiltonian just evaluated in any of the two states 1 or 2—appearing in Eq. (3), to obtain,

$$\begin{aligned} E^- \langle n_2 j_2 \epsilon_2 | f(r) | n_1 j_1 \epsilon_1 \rangle &= \langle n_2 j_2 \epsilon_2 | H_2 f(r) - f(r) H_1 | n_1\, j_1 \epsilon_1 \rangle \\ &= -ic \langle n_2\, j_2 \epsilon_2 | \alpha_r \left(f'(r) + \frac{\Delta_{21}^-}{2r} \beta f(r) \right) | n_1\, j_1 \epsilon_1 \rangle, \end{aligned} \tag{6}$$

where the primes are used to indicate r-derivatives and we have introduced the symbols $\Delta_{21}^\pm \equiv \epsilon_2(2j_2+1) \pm \epsilon_1(2j_1+1)$ and $E^\pm \equiv E_2 \pm E_1$, —in Eq. (4) only Δ_{21}^- and E^- are used, Δ_{21}^+ and E^+ will be used later on. Then computing the matrix element of $H_2\xi(r) - \xi(r)H_1$, we get [37,38]

$$\begin{aligned} &(E^-)^2 \langle n_2\, j_2\, \epsilon_2 | f(r) | n_1\, j_1\, \epsilon_1 \rangle = \\ &\langle n_2\, j_2\, \epsilon_2 | - \frac{\Delta_{21}^-}{2r^2} \beta f(r) - f''(r) - \frac{\Delta_{21}^-}{2r} f'(r) \beta - \frac{\Delta_{21}^-}{r} f(r) \beta \frac{d}{dr} + \\ &\frac{\Delta_{21}^+}{2r} f'(r) \beta + \left(\frac{\Delta_{21}^-}{2r} \right)^2 f(r) + 2i \alpha_r \beta m \left(f'(r) + \frac{\Delta_{21}^-}{2r} \beta f(r) \right) | n_1\, j_1\, \epsilon_1 \rangle, \end{aligned} \tag{7}$$

This formula is the relativistic extension of the non relativistic second hypervirial introduced in a previous work [41]. Notice that though the non relativistic hypervirial

sufficed in determining the non relativistic recurrence relation it is not so in the relativistic case, we will also need the following two results:

First,

$$E^+E^-\langle n_2\, j_2\, \epsilon_2|r^\lambda|n_1\, j_1\, \epsilon_1\rangle = \langle n_2\, j_2\, \epsilon_2|c^2\left[\frac{\Delta_{21}^-\Delta_{21}^+}{4}+\frac{\Delta_{21}^-}{2}(1-\lambda)\beta\right]r^{\lambda-2}+ \\ 2Z\left[ic\alpha_r r^{\lambda-2}(1-\lambda)-E^-r^{\lambda-1}\right]-E^+\lambda ic\alpha_r r^{\lambda-1}|n_1\, j_1\, \epsilon_1\rangle. \tag{8}$$

were, for obtaining this relation we essentially repeat the steps leading to (7) excepting that, at the end, we evaluate the result on $H_2\xi(r)+\xi(r)H_1$.

Second, we will also need

$$\left(E^- - \frac{4c^2\lambda}{\Delta_{21}^-}\right)\langle n_2\, j_2\, \epsilon_2|(-i\alpha_r r^{\lambda-1})|n_1\, j_1\, \epsilon_1\rangle = \\ \langle n_2\, j_2\, \epsilon_2| - c(\lambda-1)r^{\lambda-2} - \frac{4c}{\Delta_{21}^-}E^-r^\lambda + c\frac{\Delta_{21}^+}{2}\beta r^{\lambda-2}|n_1\, j_1\, \epsilon_1\rangle; \tag{9}$$

the detailed steps for obtaining (9) can be found in [38]. In Eqs. (8) and (9) and in most of what follows, we have explicitly used $f(r)=r^\lambda$ and $V(r)=-Z/r$.

The first of the recurrence relations we are after follows from eliminating the two terms, $2iE^+\lambda c\alpha_r r^{\lambda-1}$ and $2ic\alpha_r r^{\lambda-2}$, from (7) and (8). In this way we may get

$$c_0\langle n_2\, j_2\, \epsilon_2|r^\lambda|n_1\, j_1\, \epsilon_1\rangle = \sum_{i=1}^{3} c_i\,\langle n_2\, j_2\, \epsilon_2|r^{\lambda-i}|n_1\, j_1\, \epsilon_1\rangle + \sum_{i=2}^{3} d_i\,\langle n_2\, j_2\, \epsilon_2|\beta r^{\lambda-i}|n_1\, j_1\, \epsilon_1\rangle, \tag{10}$$

where the numbers c_i, $i=0,\ldots 3$, are given by

$$c_0 = \frac{E^+(E^-)^2\Delta_{21}^-}{D}, \\ c_1 = -\frac{2Z(E^-)^2\Delta_{21}^-}{D+4c^2}, \\ c_2 = c^2\frac{\Delta_{21}^-\Delta_{21}^+}{4} - \frac{c^2\Delta_{21}^-\lambda(\lambda-1)E^+}{D}, \\ c_3 = \frac{-2Zc^2(\lambda-1)(\lambda-2)\Delta_{21}^-}{D+4c^2}, \tag{11}$$

and the numbers d_i, $i=2$ and 3, by

$$d_2 = c^2\frac{\Delta_{21}^-}{2}\left[(1-\lambda)+\frac{\lambda E^+\Delta_{21}^+}{D}\right], \\ d_3 = \frac{Zc^2(\lambda-1)\Delta_{21}^-}{Q}. \tag{12}$$

where, for the sake of conciseness, we introduced the symbols

$$D = \Delta_{21}^{-} E^{-} - 4c^2\lambda, \qquad Q = \frac{\Delta_{21}^{-} E^{-} - 4c^2(\lambda - 1)}{\Delta_{21}^{+}}. \tag{13}$$

The second recurrence relation can be obtained from (8) through the simple but somewhat contrived process explained in [38], that yields

$$\begin{aligned} e_0\langle n_2\, j_2\, \epsilon_2|\beta r^{\lambda}|n_1\, j_1\, \epsilon_1\rangle = b_0\langle n_2\, j_2\, \epsilon_2|r^{\lambda}|n_1\, j_1\, \epsilon_1\rangle + b_2\langle n_2\, j_2\, \epsilon_2|r^{\lambda-2}|n_1\, j_1\, \epsilon_1\rangle \\ + e_1\langle n_2\, j_2\, \epsilon_2|\beta r^{\lambda-1}|n_1\, j_1\, \epsilon_1\rangle + e_2\langle n_2\, j_2\, \epsilon_2|\beta r^{\lambda-2}|n_1\, j_1\, \epsilon_1\rangle, \end{aligned} \tag{14}$$

where the numbers b_r and e_r, $r = 0, 2, 3$, are given by

$$\begin{aligned} b_0 =& 4\lambda\left[(E^{-})^2 - 4c^4\right], \\ b_2 =& c^2(1-\lambda)\left[(\Delta_{21}^{-})^2 - 4\lambda^2\right], \\ e_0 =& 2E^{+}D, \\ e_1 =& -4ZD, \\ e_2 =& c^2\frac{\Delta_{21}^{+}}{2}[(\Delta_{21}^{-})^2 - 4\lambda^2]. \end{aligned} \tag{15}$$

Of course, the energy eigenvalues are those of the relativistic hydrogen atom, namely

$$E_a \equiv E_{n_a\, j_a} = c^2\left(1 + \frac{Z^2\alpha_F^2}{\left(n_a - j_a - 1/2 + \sqrt{(j_a+1/2)^2 - Z^2\alpha_F^2}\right)^2}\right)^{-1/2}, \tag{16}$$

where $\alpha_F = 1/c \simeq 1/137$ is the fine structure constant. Please note that contrary to what it was implied in [37,38] the recurrence relations (8) and (12) remain valid even in the limit when Δ^{-} vanishes.

The new recurrence relations

Relations (9) and (12) can be useful for different computations, but they could be even more so if we could disentangle the matrix elements of r^a from the matrix elements of βr^b. This can be achieved with the help of the following relationship

$$\begin{aligned} &\langle n_2\, j_2\, \epsilon_2|\frac{\Delta_{21}^{+}}{2r}f(r)|n_1\, j_1\, \epsilon_1\rangle = \\ &\qquad \langle n_2\, j_2\, \epsilon_2|\left[\frac{\left(\Delta_{21}^{+} + \Delta_{21}^{-}\right)}{4rc^2}\left[E^{+} - 2V(r)\right] - \frac{1}{r}\right]\beta f(r) + \beta f'(r)|n_1\, j_1\, \epsilon_1\rangle; \end{aligned} \tag{17}$$

as follows from equation (8) by using the above illustrated technique but with different substitutions. Notice that we have reverted to an arbitrary radial function

$f(r)$ and a generic radial potential $V(r)$. Now using, as we did before, the specific function $f(r) = r^\lambda$ and the Coulomb potential $V(r) = -Z/r$, we obtain the *useful new relationship*

$$g_0\langle n_2\, j_2\, \epsilon_2|r^\lambda|n_1\, j_1\, \epsilon_1\rangle = j_0\langle n_2\, j_2\, \epsilon_2|\beta r^\lambda|n_1\, j_1\, \epsilon_1\rangle + j_1\langle n_2\, j_2\, \epsilon_2|\beta r^{\lambda-1}|n_1\, j_1\, \epsilon_1\rangle; \qquad (18)$$

where

$$\begin{aligned} g_0 =& \Delta_{21}^+/2, \\ j_0 =& \frac{E^+}{4c^2}(\Delta_{21}^+ + \Delta_{21}^-) + (\lambda - 1), \\ j_1 =& \frac{Z}{2c^2}(\Delta_{21}^+ + \Delta_{21}^-). \end{aligned} \qquad (19)$$

Equation (18) is fundamental for the disentanglement of the recurrence relations (10) and (14).

Let us explain now the process for disentangling the matrix elements of r^λ from those of βr^λ. We first obtain $\langle n_2\, j_2\, \epsilon_2|r^\lambda|n_1\, j_1\, \epsilon_1\rangle$ from equation (16) and from equation (14); by equating the resulting expressions, we get the recurrence relation for terms of the form $\langle n_2\, j_2\, \epsilon_2|\beta r^\lambda|n_1\, j_1\, \epsilon_1\rangle$, as

$$\eta_0\langle n_2\, j_2\, \epsilon_2|\beta r^\lambda|n_1\, j_1\, \epsilon_1\rangle = \sum_{i=1}^{3} \eta_i\langle n_2\, j_2\, \epsilon_2|\, \beta r^{\lambda-i}\, |n_1\, j_1\, \epsilon_1\rangle, \qquad (20)$$

where the constants $\eta_a,\ a = 0, 1, 2, 3$, appearing in (19) are

$$\begin{aligned} \eta_0 =& \frac{E^+ D}{2\lambda((E^-)^2 - 4c^4)} - \frac{R}{2c^2} - \frac{2\lambda}{\Delta_{21}^+}, \\ \eta_1 =& Z\frac{R}{c^2} - Z\frac{D}{\lambda((E^-)^2 - 4c^4)}, \\ \eta_2 =& \left[\frac{(\lambda-1)}{2\lambda}\frac{4\lambda^2 - (\Delta_{21}^-)^2}{(E^-)^2 - 4c^4)}\right]\left[\frac{E^+ R}{4} + \frac{c^2(\lambda-2)}{\Delta_{21}^+} - \frac{c^2\Delta_{21}^-}{4(\lambda-1)}\right], \\ \eta_3 =& \frac{Z(\lambda-1)R}{4\lambda}\left[\frac{4\lambda^2 - (\Delta_{21}^-)^2}{(E^-)^2 - 4c^4}\right]. \end{aligned} \qquad (21)$$

Equation (20) is, together with the definitions (21), the new recursion for matrix elements involving just $\beta\, r^b$.

To obtain the recursion for the matrix elements of r^a, we start with equations (10) and (18). We first obtain the three $\langle n_2\, j_2\, \epsilon_2|\beta r^{\lambda-i}|n_1\, j_1\, \epsilon_1\rangle$ $(i = 0, 1, 2)$ terms from them; next we succesively substitute them into equation (14) and, by juggling with the resulting equations, we are able to obtain

$$\nu_0\langle n_2\, j_2\, \epsilon_2|r^{\lambda}|n_1\, j_1\, \epsilon_1\rangle = \sum_{i=1}^{5} \nu_i\, \langle n_2\, j_2\, \epsilon_2|r^{\lambda-i}|n_1\, j_1\, \epsilon_1\rangle \tag{22}$$

where the constants appearing in (22) are

$$\begin{aligned}
\nu_0 =& 2(E^+E^-)^2\frac{Q}{Zc^2(\lambda-1)},\\
\nu_1 =& -8E^+(E^-)^2\frac{(Q+6c^2)}{c^2(\lambda-1)},\\
\nu_2 =& \frac{2\lambda T}{Z}\left[\frac{\lambda E^+}{(\lambda-1)W}-Q-E^+-\frac{4c^2(\lambda-2)}{\Delta_{21}^+ + \Delta_{21}^-}\right]-\frac{E^+}{Z}D\left[\frac{U}{2}-\frac{2c^2}{R}\right]-\\
& \frac{J}{Zc^2(\lambda-1)}\left[8Z^2(E^-)^2W+\frac{c^2}{2}E^+(E^-)^2\frac{4\lambda^2-(\Delta_{21}^-)^2}{QW}\right],\\
\nu_3 =& -D\left[U-\frac{4c^2}{R}\right]-4E^+(\lambda-2)QW-\frac{(E^-)^2\left(4\lambda^2-(\Delta_{21}^-)^2\right)}{(\lambda-1)},\\
\nu_4 =& \frac{c^2(\lambda-1)\left(4\lambda^2-(\Delta_{21}^-)^2\right)}{2Z}\left[\frac{\lambda E^+}{(\lambda-1)W}-Q-E^+-\frac{4c^2(\lambda-2)}{\Delta_{21}^+ + \Delta_{21}^-}\right]-\\
& 8Z(\lambda-2)QW-\frac{c^2\Delta_{21}^+}{2Z}\left(4\lambda^2-(\Delta_{21}^-)^2\right)\left[\frac{U}{4}-\frac{c^2}{R}\right],\\
\nu_5 =& c^2(\lambda-2)\left(4\lambda^2-(\Delta_{21}^-)^2\right).
\end{aligned} \tag{23}$$

Again for the sake of conciseness, we have introduced the following definitions

$$\begin{aligned}
Q =& \frac{\Delta_{21}^-E^- - 4c^2(\lambda-1)}{\Delta_{21}^+}, & R =& \frac{\Delta_{21}^+ + \Delta_{21}^-}{\Delta_{21}^+},\\
T =& \left((E^-)^2-4c^4\right), & W =& \frac{\Delta_{21}^-E^- - 4c^2\lambda}{\Delta_{21}^-E^- - 4c^2(\lambda-1)},\\
U =& \left[\frac{\{\Delta_{21}^-E^- - 4c^2(\lambda-1)\}[4\lambda(\lambda-1)E^+ - \Delta_{21}^+(\Delta_{21}^-E^- - 4c^2\lambda)]}{(\Delta_{21}^-E^- - 4c^2\lambda)(\lambda-1)\Delta_{21}^+}\right].
\end{aligned} \tag{24}$$

Equation (22) is the recursion involving only matrix elements of r^a.

The new recurrence relations are equations (20) and (22), we also think that equation (19) can be found useful in certain applications. We must also pinpoint that the relationships derived are valid in general for complex values of the exponent λ, as long as $\omega_1+\omega_2+|\lambda| > -1$, were the numbers ω_i are defined as $\sqrt{(j_i+1/2)^2-Z^2\alpha_F^2}$. This property was established in [38].

A relation for two-center integrals.

The recurrence relations established above for relativistic hydrogenic states is sufficiently general for performing many calculations. It is not however useful for

calculations involving matrix elements of a radial function between states represented by radial eigenstates corresponding to different potential functions, that is, the so-called two center matrix elements. It is the purpose of this section to present one such relation for relativistic two-center matrix elements that can be regarded as a first step in the appropriate direction. This will be done using ideas developed in [38,41,43].

General hypervirial results, the virial theorem, and other algebraic techniques [25,26,44] have been always very useful for calculating matrix elements, nonetheless they have been little used in relativistic calculations (but see [37,44,45]). We want to show here that they can have comparable importance than in non-relativistic quantum calculations. So, let us consider two radial Dirac Hamiltonians [as in equation (3)] with two possibly different radial scalar potentials $V_1(r)$ and $V_2(r)$—we are thinking on potentials like those describing vibrational states in a molecule—

$$\begin{aligned} H_1 =& c\alpha_r[p_r - i\beta\epsilon_1(j_1+1/2)/r] + \beta c^2 + V_1(r), \\ H_2 =& c\alpha_r[p_r - i\beta\epsilon_2(j_2+1/2)/r] + \beta c^2 + V_2(r), \end{aligned} \tag{25}$$

a further assumption we make is that the two potentials are displaced from their respective equilibrium points by a constant quantity, *i. e.* $r_1 + r_2 = a$, where r_i is the equilibrium position of potential $V_i(r)$ and a the displacement. Notice that, at difference with equation (3), here the numerical label in the Hamiltonians is not just convenient but has a definite physical meaning, for H_2 and H_1 refer to two in principle different systems.

Taking the difference between the Hamiltonians (25), $H_1 - H_2$, we get

$$H_1 = H_2 + ic\alpha_r\beta\frac{\Delta_{21}^-}{2r} - \left(V_2(r) - V_1(r)\right). \tag{26}$$

On employing (25), we can inmediately evaluate the commutator

$$[H_1, f_2(r)] = -ic\alpha_r\frac{df_2(r)}{dr} \tag{27}$$

where $f_2(r)$ is an arbitrary radial function and $[H, f(r)]$ stands for the commutator between H and $f(r)$. We can calculate this commutator again, but now using expression (26) to get the alternative form

$$[H_1, f_2(r)] = H_2 f_2(r) - f_2(r)H_1 - (V_2 - V_1)\, f_2(r) + ic\alpha_r\beta\frac{\Delta_{21}^-}{2r} f_2(r). \tag{28}$$

If we now equal (28) with (27) and take matrix elements of the resulting expression between the two states, $\langle n_1\, j_1\, \epsilon_1|$ and $|n_2\, j_2\, \epsilon_2\rangle$ —which correspond to the different Hamiltonians (25)— we directly obtain the hypervirial inspired relation

$$
\begin{aligned}
(E_2 - E_1)\langle n_1\, j_1\, \epsilon_1|f_2(r)|n_2\, j_2\, \epsilon_2\rangle &= \langle n_1\, j_1\, \epsilon_1|\,(V_2 - V_1)\, f_2(r)|n_2\, j_2\, \epsilon_2\rangle \\
-ic\langle n_1\, j_1\, \epsilon_1|\alpha_r &\left(f_2'(r) + \beta\frac{\Delta_{21}^-}{2r} f_2(r)\right)|n_2\, j_2\, \epsilon_2\rangle;
\end{aligned}
\tag{29}
$$

notice, however, that the energy eigenvalues in (29) refer to the different Hamiltonians (26), and not to different states of the same Hamiltonian—as was the case analysed in the first section of the paper [compare with equation (6)]. In fact, if we consider the same potentials in equation (29), *i. e.* we take $V_2(r) = V_1(r)$, we are also inmediately setting $E_1 = E_2$ and thus we recover the relationship (6), which is valid for just one center.

The important point is that equation (29) is an exact relation valid for the calculation of two center matrix elements, given as a function of the eigenenergies for any two scalar radial potentials $V_i(r)$ in the Dirac equation, and thus it can be useful for deriving recurrence relations between such matrix elements. But this is still a work in progress.

Acknowledgements.

This work has been partially supported by CONACyT. This work owes a great deal to thoughtful comments and suggestions of our colleague and friend C. Cisneros. ACI-L and MNV-M want to thank J. Morales for what they have learnt from him. F. C. Bonito, L. S. Micha, L. Bidsi, C. F. Quimo, C. Sabi, M. Botitas, F. C. Bieli, and all the gang are also acknowledged with thanks for their playful enthusiasm. This paper is dedicated to the memory of M. Osita.

References.

[1] Cohen-Tannoudji, C.; Dupont-Roc, J.; Grynberg, G. Atom-Photon Interactions; John Wiley: New York, 1992.

[2] Drake, G. W. F. Atomic, Molecular, and Optical Physics Handbook; AIP: Woodbury New York, 1996.

[3] Craig, D. P.; Thirunamachandran, T. Molecular Quantum Electrodynamics; Academic: London, 1984.

[4] Wong, M. K. F.; Yeh, H-Y. Phys Rev A 1983, 27, 2300–2304.

[5] Dobrovolska, I. V.; Tutik, R. S. Phys Lett A 1999, 260, 10–16.

[6] Löwdin, P. O. Phys Rev 1955, 97, 1474–1489.

[7] Löwdin, P. O. Phys Rev 1955, 97, 1490–1508.

[8] Löwdin, P. O.; Appel, K.; Phys Rev 1956, 103, 1746–1755.

[9] Shull, H.; Löwdin, P. O. Phys Rev 1958, 110, 1466–1467.

[10] Löwdin, P. O. Rev Mod Phys 1960, 32, 328–334.

[11] Löwdin, P. O. Rev Mod Phys 1962, 34, 80–86.

[12] Löwdin, P. O. Rev Mod Phys 1962, 34, 520–530.

[13] Löwdin, P. O. Phys Rev 1965, 139, A357–A372.

[14] Löwdin, P. O. Rev Mod Phys 1967, 39, 259–287.

[15] LaJohn, L. A.; Christiansen, P. A.; Ross, R. B.; Atashroo, T.; Ermler, W. C. J Chem Phys 1987, 87, 2812–2824.

[16] Ley-Koo, E.; Jáuregui, R.; Góngora-T, A.; Bunge, C. F. Phys Rev A 1993, 47, 1761–1770.

[17] Chi, H.; Huang, K.; Cheng, K. T. Phys Rev A 1991, 43, 2542–2545.

[18] Bethe, H. A.; Salpeter, E. E. Quantum Mechanics of One- and Two-Electron Atoms; Academic: New York, 1957.

[19] Kim, Y-K. Phys Rev 1965, 140, A1498–A1504.

[20] Martínez-y-Romero, R. P. Am J Phys 2000, 68, 1050–1055.

[21] De Lange, O. L.; Raab, R. E. Operator Methods in Quantum Mechanics; Clarendon: Oxford, 1991.

[22] Moss, R. E. Advanced Molecular Quantum Mechanics; Chapman and Hall: London, 1972.

[23] Davis, L. Phys Rev 1939, 56, 186–187.

[24] Kim, Y-K. Phys Rev 1967, 154, 17–39.

[25] Fernández, F. M.; Castro, E. A. Hypervirial Theorems; Springer: New York, 1987.

[26] Fernández, F. M.; Castro, E. A. Algebraic Methods in Quantum Chemistry and Physics; CRC: Boca Raton, 1996.

[27] Picard, J.; de Irraza, C.; Oumarou, B.; Tran Minh, N.; Klarsfeld, S. Phys Rev A 1991, 43, 2535–2537.

[28] Núñez-Yépez, H. N.; López-Bonilla, J.; Navarrete, D.; Salas-Brito, A. L. Int J Quantum Chem 1997, 62, 177–183.
[29] Morales, J; Peña, J. J.; Portillo, P.; Ovando, G.; Gaftoi, V. Int J Quantum Chem 1997, 65, 205–211.
[30] Palting, P. Int. J Quantum Chem 1998, 67, 343–357.
[31] Palting, P.; Villa, M.; Chiu, N. Y. J Mol Struct-Teo Chem 1999, 493, 51–62.
[32] Wong, M. K. F.; Yeh, H-Y. Phys Rev A 1983, 27, 2305–2310.
[33] Kobus, J.; Karkwowski, J.; Jaskólski, W. J Phys A: Math Gen 1987, 20, 3347–3352.
[34] Shabaev, V. M. J Phys B: At Mol Opt Phys 1991, 24, 4479–4488.
[35] Grant, I. P.; in Drake, G. W. F. (Editor) Atomic, Molecular and Optical Physics Handbook; American Institute of Physics: Woodbury, 1996; Chapter 32.
[36] Martínez-y-Romero, R. P. Am. J. Phys. 2000, 68, 1050–1055.
[37] Martínez-y-Romero, R. P.; Núñez-Yépez, H. N.; Salas-Brito, A. L. J Phys B: At Mol Opt Phys 2000, 33, L1–L8.
[38] Martínez-y-Romero, R. P.; Núñez-Yépez, H. N.; Salas-Brito, A. L. J Phys B: At Mol Opt Phys 2001, 34, 1261–1276.
[39] Shertzer, J. Phys Rev A 1991, 44, 2832–2835.
[40] Bessis, N.; Bessis, G.; Roux, D. Phys Rev A 1985, 32, 2044–2050.
[41] Núñez-Yépez, H. N.; López-Bonilla, J.; Salas-Brito, A. L. J Phys B: At Mol Opt Phys 1995, 28, L525–L529.
[42] Blanchard, P.; J Phys B: At Mol Phys 1974, 7, 993–1005.
[43] Morales, J. Phys Rev A 1987, 36, 4101–4103.
[44] de Lange, O. L.; Raab, R. E. Operator Methods in Quantum Mechanics; Clarendon: Oxford, 1991.
[45] Lucha, W.; Schöberl F. F.; Phys Rev Lett 1990, 23, 2733–2735.